

# PATENT SPECIFICATION

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(54) DEEP-DRAWING OF METALS COATED WITH A THERMOPLASTIC RUBBER/OIL DISPERSION

(71) We, SHELL INTERNATIONAL RESEARCH MAATSCHAPPIJ B.V., a company organized under the laws of the Netherlands, of 30, Carel van Bylandtlaan, The Hague, the Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

5 This invention relates to the non-destructive deformation, in particular deep-drawing, of metals, in particular steel.

10 Metals which are to be subjected to such deformation are usually treated with materials acting as lubricants, such as soft metals, greases, soaps, lubricating oils, solutions or dispersions of non-elastomeric polymers such as polyacrylates in volatile hydrocarbons, in order to prevent mechanical damage at the drawing levels usually applied. Some of these lubricants can also serve as preservatives, if applied to metal sheets which will be stored for some time prior to being deformed.

15 An important problem in the deep-drawing of metals is the stress distribution in the resulting shaped articles, which in heavily stretched areas may even cause the material to break. Further, for optimum results, it is desirable that the extension of the metal be uniform in all directions. With the lubricating materials normally used it is difficult to solve these problems, especially at high degrees of stretching.

20 An object of the present invention is to provide an improved method of non-destructively deforming metals, in particular steel.

25 According to the present invention there is provided a method of non-destructively deforming a metal, which comprises applying to the surface thereof a lubricant comprising a suspension, in a non-volatile (as herein defined) hydrocarbon oil, of a thermoplastic rubber which is a block copolymer having the formula  $A\leftarrow B\rightarrow A\right)_n$  or  $A\leftarrow B\leftarrow B\rightarrow A\right)_n$ , 30 wherein n is an integer, A is a non-elastomeric polymer block of a mono-alkenyl-arene and B is an elastomeric block of a conjugated diene

or a partially or completely hydrogenated block of a conjugated diene, and thereafter subjecting the metal to a deforming operation.

35 For the purposes of this specification the term "non-volatile" hydrocarbon oil is defined herein as a hydrocarbon oil having a volatility which is substantially equal to or less than that of a hydrocarbon spindle oil.

40 The lubricant used in carrying out the present invention may also comprise a volatile oil or a volatile liquid hydrocarbon such as toluene, the term "volatile" in this respect signifying a volatility which is appreciably greater than that of said non-volatile hydrocarbon oil.

45 Said thermoplastic rubbers are block copolymers having either a linear or a branched configuration, those represented by the general formula:  $A\leftarrow B\rightarrow A\right)_n$ , being the linear block copolymers and those represented by the general formula:  $A\leftarrow B\leftarrow B\rightarrow A\right)_n$ , being the branched or radial type of block copolymer. In either formula the subscript n is an integer which can be 1 to 5, for example 1. The simplest block copolymer will, therefore, have the general configuration  $A\leftarrow B\rightarrow A$ , each A representing a non-elastomeric polymer block of a monoalkenyl-arene and B representing an elastomeric block of a conjugated diene. The block(s) B may have been partially or completely hydrogenated. Preferred copolymers are those based on polystyrene (A) and polybutadiene or polyisoprene (B) blocks. The block molecular weights are variable, but the blocks A usually have number average molecular weights between 2,000 and 100,000 and the blocks B between 25,000 and 1,000,000.

50 Said thermoplastic rubbers containing fillers, oils, anti-oxidants, stabilizers and plasticizers are also suitable for the purpose of this invention.

55 The thermoplastic rubbers in the form of a crumb, granulate or powder or as concentrate in an aromatic solvent, such as toluene are mixed with the non-volatile hydrocarbon oil. This oil, which preferably is a low-viscosity lubricating oil, e.g. a spindle oil, should be of

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the paraffinic or naphthenic type if the thermoplastic rubber contains polystyrene blocks. Preferably, the content of aromatics is then below 40% w, such as below 20% w, in particular below 10% w. The dispersions obtained 5 preferably contain 1—75% w, e.g., 5—50% w, in particular 5—25% w of the thermoplastic rubber based on the total amount of thermoplastic rubber and oil.

10 The viscosity of such dispersions should, preferably, be low enough to make conventional application during sheet steel manufacture possible, although they can be diluted with volatile oils, if necessary.

15 The steel sheets may be coated, e.g., by spraying, dipping or brushing with the present dispersions or with the diluted dispersions to form an ultimate layer on said sheets having a thickness of at least 1 micron, preferably 20 5—400, e.g., 5—200 microns. During storage of the sheets corrosion will be prevented, whereas during deep-drawing of the sheets this coating functions as deep-drawing lubricant. A special preservative oil is then no longer necessary.

25 During deep-drawing the present dispersions effect a uniform stress distribution, thus preventing breakage, and provide uniform elongation of the metal in all directions.

30 The present dispersions can readily be removed using normal cleaning agents.

The present invention is illustrated by the following Example:

EXAMPLE.

35 Dispersions of a thermoplastic rubber according to the invention, namely a polystyrene/polybutadiene/polystyrene block copolymer, molecular weights 14,000/64,000/14,000, (polymer A) in a conventional 40 paraffinic/naphthenic extender oil of spindle oil viscosity, were made and compared with:

Oil B, a conventional deep-drawing pure lubricating oil containing no polymer;

Oil C, a commercially available deep-drawing lubricant being a suspension of a polyacrylate, in a lubricating oil,

with untreated sheets, and

with polymer A per se.

The dispersions according to the invention were dissolved in toluene and the solution was applied in sufficient amounts to the steel test sheets to give a coating thickness of 10 microns. The reference oils were also applied in sufficient amounts to give a coating thickness of 10 microns.

50 The thickness of the steel sheet was 0.75 mm.

The following tests were carried out.

*Swift cupping test* (deep-draw force).

A circular metal sheet, coated on both sides, is clamped between a holder and a drawing ring. A metal cup is formed by punching. During punching the material is allowed to flow from between the clamps through the ring with the result that the thickness of the cup is about equal to that of the original sheet. In this test the punching force is a measure for the effectiveness of the lubricant used; the lower the force, the better.

*Erichsen test* (stretch-draw depth).

A circular metal sheet, coated on one side, is clamped between a holder and a drawing ring, but with a high force, which keeps the sheet in position during deformation. All surface increases during deformation have therefore to be provided by the metal sheet itself, resulting in reduced thickness and ultimately in breakage. The greater the drawing depth at break, the better the performance according to this test.

Results

Polymer A	pbw	100	75	50	25	0	Oil	Oil	Untreated
Extender oil	pbw	0	25	50	75	100	B	C	„
Deep draw force	tons	4.1	3.9	3.6	3.5	4.8	4.7	4.2	4.8
Stretch draw depth	mm	11.9	11.8	11.8	11.9	10.4	10.5	10.9	10.4

From this Table it follows that especially as to deep draw force the present dispersions, in particular those containing less than about 50% of polymer A, are superior to the commercially available lubricants and polymer A per se.

WHAT WE CLAIM IS:—

1. A method of non-destructively deforming a metal, which comprises applying to the surface thereof a lubricant comprising a suspension, in a non-volatile (as herein defined) hydrocarbon oil, of a thermoplastic rubber

which is a block copolymer having the formula A-(B-A)<sub>n</sub> or A-B-(B-A)<sub>n</sub>, wherein n is an integer, A is a non-elastomeric polymer block of a mono-alkenyl-arene and B is an elastomeric block of a conjugated diene or a partially or completely hydrogenated block of a conjugated diene, and thereafter subjecting the metal to a deforming operation.

5. A method as claimed in claim 1, wherein n is 1 to 5.

10. A method as claimed in claim 1, wherein n=1.

11. A method as claimed in claim 2, wherein n=1.

12. A method as claimed in claim 2 or claim 3, wherein A is a polystyrene block and B is a polybutadiene or polyisoprene block.

15. A method as claimed in any one of claims 2-4, wherein A has a molecular weight between 2,000 and 100,000 and B has a molecular weight between 25,000 and 1,000,000.

20. A method as claimed in any one of claims 1-5, wherein the oil is a paraffinic or naphthenic oil.

25. A method as claimed in any one of claims 1-6, wherein the proportion of thermoplastic rubber is 1-75%w, based on the total amount of thermoplastic rubber and oil.

30. A method as claimed in claim 7, wherein the proportion of thermoplastic rubber is 5-50%w, based on the total amount of thermoplastic rubber and oil.

35. A method as claimed in claim 8, wherein the proportion of thermoplastic rubber is 5-25%w, based on the total amount of thermoplastic rubber and oil.

40. A method as claimed in any one of claims 1-11, wherein the applied layer of lubricant on the metal surface has a thickness of 5-400 microns.

45. A method as claimed in claim 12, wherein said thickness is 5-200 microns.

46. A method as claimed in any one of claims 1-13, wherein said lubricant also comprises a volatile oil or a volatile liquid hydrocarbon such as toluene (the word "volatile" having the meaning hereinbefore defined).

50. A method as claimed in any one of claims 1-14, wherein said non-volatile hydrocarbon oil is a spindle oil.

55. A method as claimed in claim 1 and substantially as hereinbefore described with reference to the Example.

60. An article formed by non-destructively deforming a metal by the method claimed in any one of claims 1-16.

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